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METHOD OF TREATING SUBSTANCE AND APPARATUS FOR  
CARRYING OUT THE SAME

Background of the Invention

Field of the Invention

The present invention relates to a method of treating substances by applying discharge plasma to a fluid containing the substances to be treated.

- 5 The present invention also relates to an apparatus for carrying out such a substance treating method. Particularly, the present invention relates to a technique for decomposing, by discharge plasma, harmful or poisonous substances such as dioxins contained in waste gases emitted from burning systems into harmless substances or easily collectable substances.

10 Description of the Related Art

- Various kinds of harmful substances are contained in waste gases discharged from city type incinerators and large scale industrial waste treating plants. Recently, not only NOx and SOx, but also dioxins have been notified as harmful substances. It is important to emit the waste gas into the  
15 atmosphere after reducing concentrations of these harmful substances below allowable safety level.

- Heretofore, many treating methods have been developed for reducing concentrations of harmful substances in waste gases. However, in the known methods, large scale treating equipment is required, a treating  
20 efficiency is relatively low, a running cost is rather high, and a maintenance is complicated. Therefore, the known treating methods could not be effectively used. For instance, in many burning systems, electric precipitation devices are used. However, it has been made clear that the electric precipitation might be a source generating harmful dioxins. Therefore, nowadays, a bag  
25 filter has been utilized instead of the electric precipitation device. However,

the bag filter has a short life time and its maintenance is rather complicated.

In order to remove or mitigate the above mentioned demerits, there has been proposed a substance treating method, in which harmful substances are reacted with electrons generated by corona discharge or dielectric barrier discharge and are transformed or converted into harmless substances or substances which could be collected easily. Fig. 1 shows a known waste gas treating apparatus. An electrically conductive pipe 1 serving as a coaxial tubular reaction vessel is provided, a wire electrode 2 is arranged along a longitudinal axis of the pipe 1 and a pulse supply source 3 is connected across the pipe and the wire electrode to generate corona discharge within the pipe. Then, a waste gas is flowed through the pipe 1 and dioxins,  $\text{NO}_x$  and  $\text{SO}_x$  are reacted with radicals and accelerated electrons generated by the corona discharge and are decomposed into harmless substances.

Fig. 2 shows another known waste gas treating apparatus using the above mentioned pulse discharge plasma. In this apparatus, an inner pipe 4 made of a dielectric material is arranged on an inner wall of an electrically conductive outer pipe 1 and a wire electrode 2 is arranged within the inner pipe 4 along its longitudinal axis. In this apparatus, an AC voltage supply source 5 is connected across the electrically conductive outer pipe 1 and the wire electrode 2 to generate the barrier discharge.

Fig. 3 is a perspective view depicting another known waste gas treating apparatus disclosed in Japanese Institute of Electrical Engineers Theses, Hiroyuki YASUI, "Waste Gas Treating Technique with Pulse Corona Discharge", Vol. 119, No. 5, 1997. A plurality of plate electrodes 6 are arranged in parallel with each other, wire electrodes 7 are arranged between adjacent plate electrodes, and a pulse supply source 3 is connected across the plate electrodes 6 and the wire electrodes 7. A waste gas containing substances to be treated is flowed through spaces between successive plate

electrodes 6.

In the known substance treating method using the discharge plasma, the wire electrode is arranged along the longitudinal axis of the gas flow passage having a relatively large cross sectional area, and therefore the discharge plasma could not be generated uniformly along the space through which the waste gas flows. For instance, in the known apparatus shown in Fig. 1, the discharge plasma is locally produced around the wire electrode 2 as depicted in Figs. 4 and 5, and the plasma is scarcely generated near the periphery of the gas flow passage. When the discharge plasma is localized, a possibility of the reaction of given substances contained in the waste gas with electrons generated by the plasma might be decreased, and the treating efficiency becomes low. This problem also occurs in the known apparatus shown in Fig. 3 using the plate electrodes 6 and wire electrodes 7.

In the above explained known substance treating apparatuses, the pulse supply source or AC voltage supply source is connected across the two kinds of electrodes. In order to decompose dioxins contained in a waste gas, dioxins have to be reacted with electrons having substantially high energy. However, the known waste gas treating apparatuses could not efficiently generate electrons having high energy. That is to say, although an ordinary AC voltage supply source is connected across the electrodes, it is impossible to generate efficiently electrons having desired high energy.

When the AC voltage supply source is utilized, electrons having energy of about 1 eV are predominantly generated as shown by a curve A (IIF plasma) in Fig. 6, but a density of electrons having energy higher than 5 eV becomes very low. In order to decompose dioxins efficiently, electrons having energy of about 3-10 eV are effective, but a density of such high energy electrons is low. Therefore, the known apparatus using the high frequency voltage supply source could not decompose dioxins efficiently.

Moreover, in case of using the pulse supply source, in order to decompose dioxins efficiently, it is necessary to generate electrons having energy of about 3-10 eV. To this end, a voltage pulse applied across the discharge electrodes must have a sharp or steep raising edge as well as a short pulse duration. To this end, one may consider to utilize a pulse supply source including a thyatron as an active element. The pulse supply source using the thyatron has sharp raising edge, short pulse duration and large discharge current as shown in Fig. 7. However, the thyatron has several drawbacks such as large size, low power efficiency, high cost, short life time, large secular variation and cumbersome maintenance. Particularly, in the waste treating system, a power consumption is liable to be large due to the cathode heater and cost for exchanging the thyatron having a short life time becomes high.

In order to overcome the above mentioned problems, it is desired to utilize a pulse supply source having a semiconductor element as a switching element, because the semiconductor element has a high power efficiency and a very long life time. As the semiconductor switching element, use may be made of GTO (Gate Turn-off Thyristor) and IGBT (Insulated Gate Bipolar Transistor). However, GTO has a very slow raising edge and a long duration as illustrated in Fig. 8. Furthermore, electrons having a desired energy level could not be generated efficiently unless a plurality of large scale circuits including magnetic compression circuits are connected in cascade. Although IGBT can generate a pulse having a steeper raising edge and a shorter duration than GTO as shown in Fig. 9, its raising edge is not sufficiently sharp for generating electrons having high energy of about 3-10 eV with a high density, such electrons being necessary for decomposing dioxins in an efficient manner.

There has been also proposed to treat harmful substances contained

in waste gases using materials having catalysis. However, a treating efficiency is not sufficiently high, and waste gases emitted from city type incinerators and industrial waste treating plants could not be purged effectively, because such waste gases contain harmful substances with very high densities.

Recently there has been proposed to treat harmful substances using materials such as  $\text{TiO}_2$  having photocatalysis. However, this type photocatalysis needs to be excited with ultraviolet, and therefore its application is limited to outdoor such as road fence, road surface and outer wall of building. Therefore, the photocatalysis could be not be utilized for purging waste gases emitted from city type incinerators and industrial waste treating plants.

#### Summary of the Invention

The present invention has for its object to provide a novel and useful method of treating substances, in which the substances can be treated efficiently by a combination of catalysis and discharge plasma generated uniformly along a long passage through which a fluid containing the substances to be treated is flowed.

It is another object of the invention to provide a method of treating substances, in which the substances can be treated efficiently with a pulse discharge plasma which can generate electrons having a desired high energy level with a high density.

It is another object of the invention to provide a method of treating substances, in which the above mentioned pulse discharge plasma generating electrons having high energy level can be effectively produced by a semiconductor switching element.

It is still another object of the invention to provide a method of treating substances, in which a treating efficiency can be improved by exciting

a photocatalysis material with ultraviolet radiation emitted from the discharge plasma.

According to the invention, a method of treating substances comprises the steps of:

5       generating discharge plasma within an electrically insulating honeycomb structural body having a plurality of through holes by applying a discharge voltage across electrodes, at least a part of the electrodes being made of a metal having catalysis;

      flowing a fluid containing substances to be treated through said plurality  
10   of through holes formed in the honeycomb structural body; and

      treating the substances contained in the fluid by a reaction with the discharge plasma and by catalysis of at least a part of the electrodes.

According to further aspect of the invention, a method of treating substances comprises the steps of:

15       generating discharge plasma within an electrically insulating honeycomb structural body having a plurality of through holes by applying a discharge voltage across electrodes, at least a part of said honeycomb structural body being made of a material having photocatalysis;

      flowing a fluid containing substances to be treated through said plurality  
20   of through holes formed in the honeycomb structural body; and

      treating the substances contained in the fluid by a reaction with the discharge plasma and by decomposition and/or oxidation by active oxygen generated by said photocatalysis material excited with radiation emitted from the discharge plasma.

25       According to further aspect of the invention, a method of treating substances comprises the steps of:

      generating discharge plasma within an electrically insulating honeycomb structural body having a plurality of through holes by applying a discharge

voltage across electrodes, at least a part of said honeycomb structural body being made of a photocatalysis material and at least a part of the electrodes being made of a metal having catalysis;

5 flowing a fluid containing substances to be treated through said plurality of through holes formed in the honeycomb structural body; and

treating the substances contained in the fluid by a reaction with the discharge plasma, by catalysis of at least a part of the electrodes and by active oxygen generated by said photocatalysis material excited with radiation emitted from the discharge plasma.

10 The present invention also relates to an apparatus for treating substances, and has for its object to provide a substance treating apparatus which can treat particular substances efficiently, while the apparatus can be small in size, can save power, can have a long life time, and is less expensive in cost.

15 According to the invention, an apparatus for treating substances comprises:

an electrically insulating honeycomb structural body having a plurality of parallel through holes through which a fluid containing substances to be treated is flowed;

20 an electrode system for generating discharge plasma within the honeycomb structural body such that the substances contained in the fluid flowing through the through holes is reacted with the discharge plasma, at least a part of said electrode system being made of a material having catalysis; and

25 a power supply source connected to said electrode system for applying a discharge voltage to said electrode system such that the discharge plasma is generated within the through holes of the honeycomb structural body.

According to further aspect of the invention, an apparatus for



treating substances comprises:

a honeycomb structural body having a plurality of parallel through holes through which a fluid containing substances to be treated is flowed, at least a part of said honeycomb structural body being made of ceramics including a material having photocatalysis;

an electrode system for generating discharge plasma within the honeycomb structural body such that the substances contained in the fluid flowing through the through holes are reacted with the discharge plasma and said material having photocatalysis is excited with radiation emitted from the discharge plasma; and

a voltage supply source connected to said electrode system for applying a discharge voltage to said electrode system such that the discharge plasma is generated within the through holes of the honeycomb structural body.

According to further aspect of the invention, an apparatus for treating substances comprises:

an electrically insulating honeycomb structural body having a plurality of parallel through holes through which a fluid containing substances to be treated is flowed, at least a part of said honeycomb structural body being made of a material having photocatalysis;

an electrode system for generating discharge plasma within the honeycomb structural body such that the substances contained in the fluid flowing through the through holes is reacted with the discharge plasma and said material having photocatalysis is excited with radiation emitted from the discharge plasma, at least a part of said electrode system being made of a material having catalysis; and

a power supply source connected to said electrode system for applying a discharge voltage to said electrode system such that the discharge plasma is generated within the through holes of the honeycomb structural body.

In the method and apparatus for treating a substance according to the invention, gas or liquid, i.e. fluid containing substances to be treated is flowed through the through holes formed in the honeycomb structural body and the discharge plasma is generated within the through holes. Since the  
5 discharge space is defined by the through holes, the discharge plasma is generated uniformly over a whole cross section of the fluid passage, and thus the substances can be efficiently reacted with radicals and electrons generated by the discharge plasma with a high possibility. In this manner, the substance treating efficiency can be increased.

10 Furthermore, when at least a part of the electrode system for generating the discharge plasma is made of a catalysis metal such as platinum, palladium and nickel series metal, the substances to be treated can be decomposed by the reaction with electrons having lower energy level under the catalysis. In this manner, the treating efficiency can be further improved  
15 materially.

Moreover, when at least a part of the honeycomb structural body is made of a photocatalysis material, the photocatalysis material can be effectively excited with ultraviolet radiation emitted from the discharge plasma which is generated uniformly along the through holes of the  
20 honeycomb structural body. Then, active oxygen is generated, and the substances to be treated are decomposed and/or oxidized by the thus generated active oxygen. According to the invention, the active oxygen is generated not only near the inner wall of the through hole, but also over a whole cross section of the through hole, and therefore the treating efficiency is very high.

25 Further, the substances to be treated are first transformed into intermediate substances by radicals and electrons in the discharge plasma, and then the thus transformed intermediate substances are further treated by the active oxygen. Alternatively, the substances to be treated are first reacted with the active

oxygen to produce intermediate substances, and then the thus transformed intermediate substances are reacted with radicals and electrons in the discharge plasma. In this manner, the substances contained in the fluid can be treated very efficiently.

5           The method and apparatus for treating substances according to the invention may be used for various applications. Particularly, it is preferable to apply the present invention to city type waste incinerators and large scale industrial waste treating plants, and dioxins,  $\text{NO}_x$  and  $\text{SO}_x$  contained in waste gases discharged from these burning systems can be decomposed into  
10   harmless substances by the reaction with the discharge plasma generated within the honeycomb structural body. In such applications, it is particularly preferable to generate the discharge plasma within the honeycomb structural body as pulse corona discharge plasma. In such a pulse corona discharge plasma, electrons having sufficiently high energy level for effectively  
15   decomposing dioxins can be generated with an extraordinary high density. In this case, in order to decompose harmful substances such as dioxins in an effective manner, it is preferable to generate the pulse corona discharge plasma which can produce electrons having high energy level of 3-10 eV. To this end, it is preferable that a raising edge of a pulse discharge current is larger  
20   than  $5 \times 10^{10}$  A/second, particularly larger than  $1 \times 10^{11}$  A/second and an amplitude of the pulse discharge current is several thousands amperes.

          According to the invention, in order to generate the pulse corona discharge plasma, it is preferable to construct said pulse supply source by a static induction thyristor as a switching element. The static induction  
25   thyristor is a semiconductor switching element, and therefore size is small, power consumption is low, life time is semipermanent, maintenance is easy, and cost can be reduced.

          According to a first principal structure of the present invention, said

discharge plasma is generated within the honeycomb structural body in a direction parallel to a longitudinal direction of the through holes, and according to a second principal structure of the present invention, the discharge plasma is generated within the honeycomb structural body in a  
5 direction perpendicular to a longitudinal direction of the through holes.

In a preferable embodiment of the substance treating apparatus according to the first principal structure of the present invention, said electrode system comprises first and second electrodes provided on respective end surfaces of the honeycomb structural body and said first and second electrodes  
10 are connected to the power supply source such that a discharge voltage is applied in a direction parallel to a longitudinal direction of the through holes. In such a structure, said first and second electrodes may be formed by first and second mesh electrodes provided on the end surfaces of the honeycomb structural body, or may be formed by metal films applied on the end surfaces  
15 of the honeycomb structural body. In the later case, it is preferable that the metal films are extended onto inner walls of the through holes.

In a preferable embodiment of the substance treating apparatus according to the second principal structure of the present invention, said electrode system comprises a cylindrical electrode arrange on the honeycomb  
20 structural body and a plurality of wire electrodes passing through holes, said cylindrical electrode being connected to a first output terminal of the power supply source and said plurality of wire electrodes being connected to a second output terminal of the power supply source.

In another preferable embodiment of the substance treating  
25 apparatus according to the second principal structure of the invention, the electrode system comprises first and second groups of a plurality of wire electrodes passing through the through holes, said first and second groups of a plurality of wire electrodes being connected to first and second output

terminals, respectively of the power supply source.

In another preferable embodiment of the substance treating apparatus according to the second principal structure of the present invention, the electrode systems comprises a first group of a plurality of strip electrodes  
5 each being applied on inner walls of the through holes and a second group of a plurality of strip electrodes each being applied on the inner walls of the through holes to be opposed to the first group strip electrodes, said first and second groups of a plurality of wire electrodes being connected to first and second output terminals, respectively of the power supply source.

10 In case of using the honeycomb structure, it is preferable to form protrusions and depressions in inner walls of the through holes of the honeycomb structural body. Then, the fluid containing substances to be treated becomes a turbulent flow and is effectively stirred.

According to the present invention, a plurality of honeycomb  
15 structural bodies are arranged in parallel with each other or in series with each other. In the former case, electrodes arranged on one end surfaces of the honeycomb structural bodies are commonly connected to one output terminal of the power supply source and all electrodes provided on the other end surfaces of the honeycomb structural bodies are commonly connected to the  
20 other output terminal of the power supply source. In the later case, electrodes arranged on end surfaces of respective honeycomb structural bodies may be connected to a same power supply source or different power supply sources having different output voltages.

According to further aspect of the present invention, an apparatus  
25 for treating substances comprises:

a sleeve electrode;

a first insulating sleeve made of ceramics containing a material having photocatalysis and arranged in an inner wall of the sleeve electrode, said first

insulating sleeve constituting a passage for a fluid containing substances to be treated;

a wire electrode arranged along a central axis of the first insulating sleeve;

a second insulating sleeve made of ceramics containing a material having photocatalysis and arranged around the wire electrode; and

a discharge voltage source connected to said sleeve electrode and wire electrode to generate discharge plasma between the sleeve electrode and the wire electrode;

wherein the substances contained in the fluid are treated by reaction with the discharge plasma and with active oxygen generated by exciting the material having photocatalysis with radiation emitted from the discharge plasma.

Also in this substance treating apparatus, it is preferable that the discharge voltage source is formed by a pulse supply source to generate pulse corona discharge between the sleeve electrode and the wire electrode.

Furthermore, the material having photocatalysis may be  $\text{TiO}_2$ .

#### Brief Description of the Drawings

Fig. 1 is a perspective view showing schematically a known waste gas treating apparatus including a pipe-like electrode and a wire electrode;

Fig. 2 is a schematic cross sectional view illustrating a known waste gas treating apparatus utilizing a dielectric barrier discharge;

Fig. 3 is a perspective view depicting schematically a known waste gas treating apparatus utilizing corona discharge generated by plate electrodes and wire electrodes;

Figs. 4 and 5 are lateral and longitudinal cross sectional views, respectively showing a discharge condition in the known waste gas treating apparatus shown in Fig. 1;

Fig. 6 is a graph showing a relationship between energy and density of electrons generated in known high frequency plasma;

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Figs. 7, 8 and 9 are graphs illustrating a waveform of pulses generated by pulse supply sources using thyatron, GTO and IGBT, respectively;

Fig. 10 is a schematic view showing a first embodiment of the substance treating apparatus based on a first principal structure according to the present invention;

Fig. 11 is a schematic view depicting a second embodiment of the substance treating apparatus based on the first principal structure according to the invention;

Fig. 12 is a graph showing a waveform of a pulse generated by a pulse supply source utilizing a static induction thyristor;

Fig. 13 is a perspective view illustrating a part of a mesh electrode of a third embodiment of the substance treating apparatus according to the invention;

Fig. 14 is a perspective view illustrating a part of a mesh electrode of a fourth embodiment of the substance treating apparatus according to the invention;

Fig. 15 is a perspective view illustrating a fifth embodiment of the substance treating apparatus according to the invention, in which mesh electrodes are applied to end surfaces of a honeycomb structural body;

Fig. 16 is a perspective enlarged view representing a part of the mesh electrode shown in Fig. 15;

Figs. 17 and 18 are lateral and longitudinal cross sectional views, respectively showing a condition of pulse corona discharge in the embodiment shown in Fig. 15;

Figs. 19, 20, 21 and 22 are schematic views illustrating sixth, seventh, eighth and ninth embodiments, respectively of the substance treating apparatus according to the invention based on the second principal structure;

Fig. 23 is a schematic perspective view illustrating a tenth embodiment of the substance treating apparatus according to the invention, in which a plurality of honeycomb structural bodies are arranged in parallel;

Fig. 24 is a schematic perspective view illustrating an eleventh embodiment of the substance treating apparatus according to the invention, in which a plurality of honeycomb structural bodies are arranged in series;

Fig. 25 is a schematic perspective view showing a twelfth embodiment of the substance treating apparatus according to the invention, in which a plurality of honeycomb structural bodies are arranged in series;

Fig. 26 is a cross sectional view depicting a thirteenth embodiment of the substance treating apparatus according to the invention, in which depressions and protrusions are formed in an inner wall of a through hole of a honeycomb structural body;

Fig. 27 is a perspective view showing a fourteenth embodiment of the substance treating apparatus according to the invention, in which a honeycomb structural body is not used; and

Fig. 28 is a schematic view representing a waste burning plant using the substance treating apparatus according to the invention.

#### Description of the Preferred Embodiments

Now the present invention will be explained in detail with reference to several embodiments shown in the accompanying drawings.

Fig. 10 is a schematic view showing a first embodiment of the substance treating apparatus according to the invention based on the first principal structure. According to the invention, a honeycomb structural body 11 made of an electrically insulating material is used as a structural member for forming a passage through which a fluid containing substances to be treated is flowed as well as a discharge space for generating discharge plasma. In the first principal structure according to the invention, a discharging voltage



is applied in parallel with a longitudinal direction in which a plurality of through holes 12 formed in the honeycomb structural body 11 extend. In the present embodiment, mesh electrodes 13 and 14 are provided on end surfaces of the honeycomb structural body 11 and an AC voltage supply source 15 is  
5 connected across these mesh electrodes 13 and 14. Furthermore, these mesh electrodes 13 and 14 are made of a material having catalysis. In the present embodiment, the mesh electrodes 13 and 14 are made of nickel series metal. According to the invention, the electrodes may be made of any metal having catalysis such as platinum and palladium. By using the mesh electrodes 13  
10 and 14 having catalysis, harmful substances contained in a fluid flowing through the through holes 12 formed in the honeycomb structural body 11 are liable to be decomposed, and therefore can be effectively decomposed by the reaction with radicals and accelerated electrons generated by the discharge plasma produced within the honeycomb structural body 11.

15 In the present embodiment, harmful substances such as dioxins,  $\text{NO}_x$  and  $\text{SO}_x$  contained in a waste gas emitted from a city type incinerator are decomposed into harmless substances by reacting these harmful substances with radicals and accelerated electrons generated in the discharge plasma which is produced within the honeycomb structural body 11. The  
20 honeycomb structural body 11 is made of cordierite ceramics and the through holes 12 are formed with a density of about five holes per one square centimeter. The mesh electrodes 13 and 14 has a mesh size of 40 mesh. Furthermore, the AC supply source 15 has a variable output voltage up to 70 kV and a frequency of several kHz, e.g. 5 kHz.

25 It should be noted that the number of the through holes 12 per unit surface area of the honeycomb structural body 11, the mesh size of the mesh electrodes 13 and 14, and an output voltage of the high frequency voltage supply source 15 as well as a cross sectional area of a through hole 12, and

length and diameter of the honeycomb structural body 11 may be determined in accordance with a flow rate of a waste gas containing substances to be treated, concentrations of these substances in the waste gas and residual concentrations of these substances after the treatment. Mainly due to  
5 manufacturing view points, the honeycomb structural body 11 preferably has a length of about 1-100 cm and a diameter of about 5-20 cm. The through hole 12 has a square cross section having such a size that its inner contact circle is preferably set to about 5-10 mm.

Fig. 11 is a schematic perspective view showing a second  
10 embodiment of the substance treating apparatus according to the invention also based on the first principal structure. In this embodiment, portions similar to those of the first embodiment are denoted by same reference numerals used in Fig. 10 and their detailed explanation is dispensed with. In the first embodiment shown in Fig. 10, the mesh electrodes made of a metal  
15 having catalysis 13 and 14 are connected to the AC supply source 15, but in the present embodiment, the mesh electrodes 13 and 14 are connected to a pulse supply source 16. By using the pulse supply source 16, pulse corona discharge plasma is generated in the through holes 12 formed in the honeycomb structural body 11. According to the invention, the pulse supply  
20 source 16 is constructed such that electrons having high energy level such as about 3-10 eV are generated with an extraordinary high density. Then, dioxins contained in a waste gas can be effectively decomposed.

As explained above, in the present invention, by using the pulse supply source 16, it is possible to generate electrons having high energy of  
25 about 3-10 eV with an extraordinary high density as represented by a curve B in Fig. 6. Such electrons having energy of about 3-10 eV can decompose dioxins in an efficient manner, and therefore an ability for treating a waste gas can be improved. Furthermore, in the present embodiment, the mesh

electrodes 13 and 14 are made of a metal having catalysis and harmful substances are liable to be decomposed. In this manner, the decomposition of harmful substances contained in the waste gas can be further improved by a synergic effect of the catalysis of the mesh electrodes and the high energy electrons generated by the pulse corona discharge plasma.

In order to generate electrons having high energy of about 3-10 eV for decomposing dioxins efficiently with a high density, the pulse supply source 16 is preferably constructed such that a raising edge of a pulse corona discharge current is higher than  $5 \times 10^{10}$  A/sec, particularly  $1 \times 10^{11}$  A/sec, an output voltage is higher than 10-70 kV and a conduction current is several thousands amperes. By using such a pulse supply source, a pulse voltage applied across the discharging electrodes can have a raising rate of about  $1 \times 10^{12}$  V/sec. Such a pulse supply source may be constructed by a thyatron, but the pulse supply source including the thyatron has various drawbacks such as large size, high power consumption, short life time, i.e.  $10^9$  shots and cumbersome maintenance and high cost.

According to the invention, in order to mitigate the above mentioned drawbacks of the pulse supply source, use is made of a pulse supply source including a static induction thyristor as a switching element. Fig. 12 is a graph showing a property of the static induction thyristor. From this graph, it is apparent that the static induction thyristor has a very steep raising edge and can conduct a very large current. Of course, the static induction thyristor is a semiconductor element, a size is small, i.e.  $\phi 50$  to  $\phi 100$  mm, a power consumption is very low, a life time is substantially semipermanent, maintenance is easy and cost is low. In this manner, the pulse supply source having the static induction thyristor as a switching element is most suitable for the pulse supply source of the substance treating apparatus according to the invention. According to the invention, the

amplitude of the pulse voltage is about 10-70 kV and a pulse repetition frequency is several kHz to 10 kHz.

Figs. 13 and 14 are perspective views showing mesh electrodes of third and fourth embodiments, respectively of the substance treating apparatus according to the invention. Also in these third and fourth embodiments, the mesh electrodes are made of a metal having catalysis. In the third embodiment shown in Fig. 13, through holes 12 of the honeycomb structural body 11 have a hexagonal cross section and the mesh electrode 13 has rectangular openings. In the fourth embodiment illustrated in Fig. 14, through holes 12 of the honeycomb structural body 11 has a square cross section and the mesh electrode 13 has a corresponding square openings so that the openings of the mesh electrode are not covered with the mesh electrode. According to the invention, it is not always necessary to make size and configuration of the mesh of the electrode 13 and the through hole 12 of the honeycomb structural body 11 to be identical with each other. It is important to construct the mesh electrode and through hole such that discharge plasma is generated uniformly over the whole structure of the honeycomb structural body.

Fig. 15 is a perspective view showing a fifth embodiment of the substance treating apparatus according to the invention based on the first principal structure, and Fig. 16 is a perspective view illustrating a mesh electrode on an enlarged scale. In the present embodiment, mesh electrodes 17 and 18 are formed by metal layers applied on end surfaces of a honeycomb structural body 11. In this manner, it is possible to obtain the mesh electrodes which do not clog through holes 12 of the honeycomb structural body 11. The mesh electrodes 17 and 18 are connected to a pulse supply source 16. In the present embodiment, the mesh electrodes 17 and 18 are extended onto inner walls of the through holes 12 to increase a contact surface

of the mesh electrodes with a waste gas.

Figs. 17 and 18 are lateral and longitudinal cross sectional views, respectively representing a condition of pulse corona discharge plasma generated along the through holes 12 of the honeycomb structural body 11 when a pulse is applied to the mesh electrodes from the pulse supply source 16. As illustrated in these figures, discharge plasma is generated uniformly along the through holes 11 of honeycomb structural body 11, and therefore dioxins contained in waste gas can be effectively reacted with high energy electrons and radicals generated by the discharge plasma. In this manner, dioxins can be decomposed effectively. The inventors have confirmed that the discharge plasma is a surface discharge produced along the inner wall of the through hole 12 formed in the honeycomb structural body 11.

In the first to fifth embodiments explained above, the discharging voltage is applied in a direction parallel to a longitudinal direction of the through holes 12 formed in the honeycomb structural body 11. In the second principal structure according to the invention, the discharging voltage is applied in a direction perpendicular to the longitudinal direction of the through holes. Fig. 19 is a perspective view showing a sixth embodiment of the substance treating apparatus according to the invention based on the second principal structure. In the present embodiment, a plurality of wire electrodes 21 are passed through the through holes 12, said wire electrodes being made of a metal having catalysis. One ends of the wire electrodes 21 are secured to a first conductive plate 22 and the other ends of the wire electrodes 21 are secured to a second conductive plate 23. The first and second conductive plates 22 and 23 are connected one of output terminals of a pulse supply source 16, and the other output terminal of the pulse power supply source is connected to a cylindrical electrode 24 arranged on the honeycomb structural body 11. In this case, it is not necessary to pass the wire electrodes 21

having catalysis through all the through holes 12. According to the invention, it is preferable to spread the wire electrodes 21 uniformly over the through holes 12.

Fig. 20 is a schematic view illustrating a seventh embodiment of the substance treating apparatus according to the second principal structure of the present invention. In the above mentioned sixth embodiment shown in Fig. 19, one the discharging electrodes is constituted by the cylindrical electrode 25 arranged around the honeycomb structure 11, but in the present embodiment, all discharging electrodes are formed by wire electrode made of a metal having catalysis and are passed through the through holes 12. That is to say, wire electrodes 26 of a first group are connected to one of output terminals of a pulse supply source 16 and wire electrodes 27 belonging to a second group are connected to the other output terminal of the pulse supply source 16. In this case, the wire electrodes 26 and 27 of the first and second groups are arranged to be distributed uniformly.

Fig. 21 is a schematic view depicting an eighth embodiment of the substance treating apparatus according to the second principal structure of the invention. In the present embodiment, a honeycomb structural body 11 is made of ceramics including  $\text{TiO}_2$  having photocatalysis. Discharging electrodes are formed by rod electrodes 28 and 29 formed by injecting a conductive material into through holes 12 of the honeycomb structural body 11. In this case, a through hole 12 having a rod electrode formed therein is completely clogged, and therefore the rod electrodes 28 and 29 are preferably distributed with a lower density than the previous embodiments.

In the present embodiment, a discharging voltage is applied in a direction perpendicular to a longitudinal direction of the through holes 12 of the honeycomb structural body 11 and discharge plasma is generated within through holes in which the rod electrodes 28 and 29 are not provided. the

photocatalysis material contained in the ceramic honeycomb 11 is excited with ultraviolet radiation emitted from the discharge plasma to produce active oxygen. Harmful substances contained in a waste gas flowing through the through holes 12 are decomposed or oxidized by active oxygen. In this case, active oxygen is generated not only near the inner walls of the through holes 12, but also apart from the inner walls. Therefore, a possibility of reaction of harmful substances in waste gas with active oxygen is increased and the treating efficiency is further improved.

Fig. 22 is a perspective view depicting a ninth embodiment of the substance treating apparatus according to the second principal structure of the present invention. In the present embodiment, a honeycomb structural body 11 is made of ceramics containing a photocatalysis material, and first and second strip electrodes 31 and 32 made of a metal having catalysis are secured on inner walls of through holes 11 formed in the honeycomb structural body 11. The first and second strip electrodes 31 and 32 are connected to a pulse supply source 16. The strip electrodes 31 and 32 may be formed by applying a suitable mask on an inner wall of a through hole, a metal having catalysis is deposited on the inner wall, and then the mask is removed. Alternatively, a metal having catalysis may be first applied on an inner wall of a through hole and then, a part of the metal film may be removed by using a suitable mask. It is preferable to provide the strip electrodes 31 and 32 in all the through holes 12, but according to the invention, it is not always necessary to do so.

In the embodiments so far explained, only a single honeycomb structural body 11 is provided, but in case of treating a large amount of a waste gas, a single honeycomb structural body could not provide a sufficiently large cross sectional area. In a tenth embodiment of the substance treating apparatus according to the invention shown in Fig. 23, a plurality of honeycomb structural bodies 11 are arranged in parallel with each other to

obtain a large cross sectional area through which a waste gas is flowed. Mesh electrodes 35 arranged on one end surfaces of respective honeycomb structural bodies 11 are commonly connected to one output terminal of a pulse supply source 16 and mesh electrodes 36 provided on the other end surfaces of honeycomb structural bodies 11 are commonly connected to the other output terminal of the pulse supply source 16. In this manner, a plurality of honeycomb structural bodies 11 are arranged in parallel with each other with respect to the flow of a waste gas to be treated as well as electrically. According to the invention, the honeycomb structural bodies 11 may be made of ceramics containing a material having photocatalysis and/or the mesh electrodes 35 and 36 may be made of a metal having catalysis.

When a concentration of harmful substances contained in a waste gas is high or an allowable residual amount of harmful substances in a treated gas must be very small, it is not sufficient to flow a waste gas through a single honeycomb structural body. In such a case, a longer honeycomb structural body may be used. However, in this case, a discharging voltage might be extremely high. In an eleventh embodiment of the substance treating apparatus according to the invention, a plurality of honeycomb structural bodies 11a, 11b, 11c and 11d are arranged in series with each other as depicted in Fig. 24. In such a tandem arrangement, mesh electrodes arranged on end surfaces of honeycomb structural bodies are alternately connected to first and second output terminals of a pulse supply source 16. Also in the present embodiment, one or more of the honeycomb structural bodies 11a, 11b, 11c and 11d may be made of ceramics containing a material having photocatalysis and/or one or more mesh electrodes may be made of a metal having catalysis.

Fig. 25 is a schematic perspective view showing a twelfth embodiment of the substance treating apparatus according to the invention, in



which a plurality of honeycomb structural bodies 11a-11f are arranged in series with each other. In the eleventh embodiment shown in Fig. 24, all the honeycomb structural bodies have the same configuration and size and the same discharging voltage is applied across end surfaces of respective

5 honeycomb structural bodies. In the present embodiment, the honeycomb structural bodies 11a-11f have different lengths and different discharging voltages are applied to the honeycomb structural bodies. That is to say, viewed in a direction of a flow of a waste gas, first two honeycomb structural bodies 11a and 11b have a short length and mesh electrodes arranged on end

10 surfaces of these honeycomb structural bodies are connected to a first pulse supply source 16a. Next two honeycomb structural bodies 11c and 11d have a long length and mesh electrodes arranged on end surfaces of these honeycomb structural bodies are connected to a second pulse supply source 16b. The remaining two honeycomb structural bodies 11e and 11f have a

15 short length and mesh electrodes arranged on end surfaces of these honeycomb structural bodies are connected to a third pulse supply source 16c.

The first two honeycomb structural bodies 11a and 11b connected to the first pulse supply source 16a constitute a preliminary exciting region for exciting preliminarily harmful substances contained in a waste gas.

20 Therefore, the mesh electrodes arranged on end surfaces of these honeycombs structural bodies 11a and 11b are made of a metal having catalysis such that harmful substances can be effectively decomposed preliminarily. The next two honeycomb structural bodies 11c and 11d constitute a main exciting region for decomposing harmful substance preliminarily excited in the

25 preliminary exciting region into harmless substances and/or substances which could be easily collected by a later simple treatment. Therefore, it is preferable to make the honeycomb structural bodies 11e and 11f of a material having photocatalysis. The remaining two honeycomb structural bodies 11e

and 11f constitute an after exciting region for decomposing residual harmful substances with electrons having higher energy. Output peak voltages of the first, second and third pulse supply sources 16a, 16b and 16c are set to 15 kV, 20 kV and 30 kV, respectively. In the present embodiment, the honeycomb structural body has through holes of square cross section having a side of 6 mm. According to the invention, size and configuration of through holes of honeycomb structural body and amplitude and pulse duration of the pulse voltage may be determined such that suitable discharge condition can be attained.

Fig. 26 is a cross sectional view showing a configuration of inner walls of through holes 12 of a honeycomb structural body 11 of a thirteenth embodiment of the substance treating apparatus according to the invention. In the previous embodiments, the through holes 11 have flat or smooth inner walls, but in the present embodiment, protrusions and depressions are formed in the inner walls of through holes 12 as illustrated in Fig. 26. Such a configuration of the inner walls of through holes 12 may be easily obtained by forming a number of ring-shaped recesses or by forming small protrusions regularly or at random. In the present embodiment, the protrusions and depressions are formed in a whole inner wall of through hole 12, but according to the invention, they may be formed in a part of the inner wall. Particularly when the honeycomb structural body 11 is made a material having photocatalysis, it is preferable to form protrusions and depressions in a whole surface of a through hole 12.

When the through holes 12 have protrusions and depressions, a waste gas is disturbed to generate a turbulent flow. Then, the waste gas is stirred effectively and a possibility of reaction of harmful substances with high energy electrons generated by the discharge plasma. In this manner, the treating efficiency can be further improved. It should be noted that the

formation of protrusions and depressions in the inner walls of through holes 12 does not substantially affect the generation of discharge plasma. Moreover, when the honeycomb structural body 11 is made of a material having photocatalysis, harmful substances are treated by decomposition and/or  
5 oxidation by active oxygen produced by the excitation with ultraviolet emitted from the discharge plasma. In this manner, the generation of the turbulent flow is advantageous.

In all the embodiments so far explained, a waste gas is flowed through the through holes formed in the honeycomb structural body and the  
10 discharge plasma is generated along the through holes. According to the invention, when the photocatalysis is utilized, it is not always necessary to use the honeycomb structural body. Now such an embodiment will be explained.

Fig. 27 is a perspective view showing schematically a fourteenth embodiment of the substance treating apparatus according to the invention.  
15 In the present embodiment, on an inner wall of a metal sleeve electrode 36 there is arranged a first insulating sleeve 37 made of ceramics including a material having photocatalysis. The first insulating sleeve 37 defines a passage for a waste gas flow. Along a center of the first insulating sleeve 37, there is further arranged a wire electrode 38 having a second insulating sleeve  
20 39 applied thereon, said second insulating sleeve being made of ceramics including a material having photocatalysis. The outer sleeve electrode 36 and wire electrode 37 are connected to a pulse supply source 16, pulse corona discharge plasma is generated between the sleeve electrode 37 and the wire electrode 38.

25 Also in the present embodiment, harmful substances contained in a waste gas are decomposed by the reaction with accelerated electrons and radicals generated by the discharge plasma between the sleeve electrode 36 and the wire electrode 38, and at the same time, harmful substances are

decomposed and/or oxidized by active oxygen produced by the first and second insulating sleeves 37 and 39 excited with ultraviolet generated by the discharge plasma. In this manner, the harmful substances can be treated efficiently.

5           Fig. 28 is a schematic view showing a waste burning plant having the substance treating apparatus according to the invention. A collected waste is burnt by a burning furnace 41 and a waste gas from the furnace is conducted to a dust collecting chamber 43 through a duct 42. During the  
10           potation through the duct 42, hydrated lime is added to the waste gas. In the dust collecting chamber 43, particles contained in the waste gas are collected. Then, the waste gas is guided into a harmful substance removing chamber 45 having the substance treating apparatus 44 according to the invention. In the harmful substance removing chamber 45, during the waste gas is flowed  
15           through the through holes in the honeycomb structural body, harmful substances in the waste gas such dioxins,  $\text{SO}_x$  and  $\text{NO}_x$  are effectively decomposed by the reaction with the discharge plasma. Since the discharging electrodes are made of a metal having catalysis and/or the honeycomb structural body is made of a material having photocatalysis, harmful substances can be processed with a very high treating efficiency.  
20           Finally, a harmless waste gas from the harmful substance removing chamber 44 is discharged from a smokestack 46.

          It should be noted that the present invention is not limited to the embodiments explained above, but many alternations and modifications may be conceived by a person skilled in the art within the scope of the invention.  
25           For instance, in the above embodiments, the substance treating technology according to the present invention is applied to city type incinerators and waste burning plants. However, the substance treating technique according to the invention may be equally applied to another applications. For instance,

the present invention may be applied to a deposition of silicon by a decomposition of silane. Furthermore, the present invention may be applied to treat flon and trichloroethylene.

As explained above in detail, according to the present invention,  
5 since the discharge plasma is generated within the through holes formed in the honeycomb structural body, the discharge plasma can be generated uniformly over a whole honeycomb structural body. Therefore, by flowing a gas containing substances to be treated through the through holes, the substances can be effectively decomposed or transformed into easily collectable  
10 substances by the reaction with electrons generated by the discharge plasma. In this manner, the given substances can be treated efficiently. Moreover, when the discharging electrodes are made of a metal having catalysis, the substances can be easily decomposed, and when the honeycomb structural body is made of a material having photocatalysis, substances can be  
15 decomposed and/or oxidized by active oxygen generated by the photocatalysis material excited with ultraviolet emitted from the discharge plasma. Then, the treating efficiency can be further improved.

When the pulse supply source is used for generating the discharge plasma, electrons having sufficiently high energy for decomposing dioxins can  
20 be generated with an extraordinary high density, and dioxins can be efficiently converted into harmless substances. Therefore, the substance treating technique according to the invention is particularly preferable to be applied to city type incinerators and large scale industrial waste treating plants.

When use is made of the pulse supply source having a static  
25 induction thyristor as a switching element, small size, low power consumption, semipermanent life time, easy maintenance, low initial cost and low running cost can be attained.

Moreover, in the embodiments in which the discharging voltage is

applied in a direction parallel to a longitudinal direction of through holes formed in a honeycomb structural body, since a large discharge region can be obtained by the surface discharge along inner walls of through holes, the reaction of substances to be treated with electrons generated by the discharge plasma is enhanced to increase a treating efficiency.

Further, the substance treating apparatus according to the invention may applied to existing waste treating plants, firepower generating stations, blast furnaces and so on, and the present invention can provide one of solutions for environmental problems and can used in various applications.